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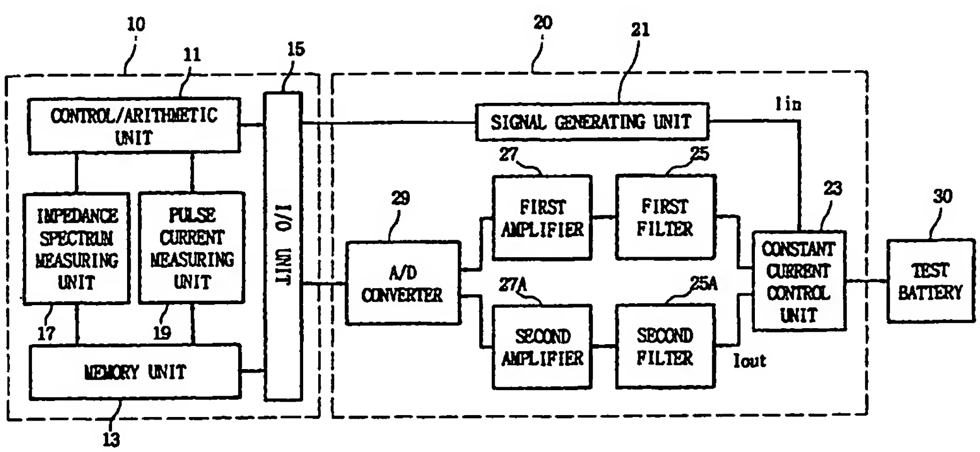

(57) Abstract

Provided with a method of measuring battery capacity using parameters obtained from a voltage response signal of a current waveform or an impedance spectrum generated thereof where the method includes the steps of: measuring voltage response signals based on a current waveform applied to a primary or secondary battery; obtaining parameters of an equivalent circuit composed of model parameters such as resistors, capacitors and transmission lines either directly from voltage response or after its conversion to frequency dependent impedance; and determining the unknown battery capacity from the voltage response characteristics based on a correlation between the measured capacity and the model parameters, which correlation is previously determined by a real-time discharge method, thereby takes a shorter time than a real-time discharge method and delivering efficiency and reliability in determining model parameters of an equivalent circuit which are in close correlation with the charge/discharge condition of the battery.

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METHOD OF AND APPARATUS FOR MEASURING BATTERY CAPACITY

Technical Field

The present invention relates to a method of and apparatus for determining an unknown capacity of a battery by applying current or voltage to a primary and secondary battery and by measuring and analyzing an output signal based on an applied input signal. More particularly, it relates to a method of and apparatus for measuring battery capacity using parameters obtained from a voltage response signal of a current wave form or an impedance spectrum generated thereof, which provide a non-destructive measurement of battery capacity, for measuring an unknown remaining capacity of a standardized battery product, or in case of a manufacturing, grading the rated capacity of the batteries.

Background Art

A general method used for measuring battery capacity includes a real-time discharge method, which is to measure the discharge time t_d for a consumption of electrical energy by the battery at a constant current I_d.

If the capacity is expressed in ampere-hour (Ah), the discharge time t_d that a battery supplies electrical energy is given by Equation 1, which is used as the standard for evaluating battery capacity, for example, the Korean Industrial Standards.

[Equation 1]

$$t_d = Ah / I_d$$

A real-time discharge method is one for measuring battery capacity in a direct way and takes a long time throughout the entire discharge period in real time.

Also, it is necessary to use a plurality of apparatuses in order to discharge

multiple batteries independently if the user has to measure plural batteries in a simultaneous manner. This results in a reduction of production efficiency in manufacturing of batteries.

Especially, for the primary battery, the real-time discharge method is inapplicable to the measurement of battery for purpose of quality control of products.

A more efficient method used for measuring battery capacity is one that enables a measurement of the battery characteristics for a short time relative to the discharge period of the battery in real-time, as a result of which precise information can be obtained concerning charge/discharge condition or remaining capacity of the battery.

In regards to the method characterizing the state of charge/discharge of battery, measurements of open circuit voltage, voltage and its variations in battery operation, output signal characteristic responsive to input voltage or current applied to battery, and thereby induced internal resistance or impedance function are generally known.

A use of these various methods provides a measurement of battery capacity for a short time relative to a real-time discharge method.

It is however necessary to provide a precise correlation between the measured value and the actual capacity in order to obtain battery capacity in the above-stated methods.

U.S. Patent No. 3,808,487 discloses a method for sensing the charge condition of a storage battery with a response signal based on a pulse signal which has been periodically applied to the battery during charging.

According to the method. information concerning the charge condition and battery capacity is not extracted from the response signal but by a detection of changes in the measured signal. which is expected at the end point of charge.

In another method stated in U.S. Patent No. 4.952.862. the remaining capacity

can be calculated from the measured voltage and the discharge characteristic which is expressed in voltage-hour function including the Peukert parameter.

Especially, EP 119,547 discloses a method used for measuring discharge voltage as a function of time and determining the discharge condition from the averaged change rate of discharge voltage in a predetermined time interval.

When calculating the capacity from a measured voltage and its variants as described above, a precision of the correlation between the measured value and battery capacity is strongly dependant upon the discharge characteristic.

For instance, a battery having a plateau of voltage provides extremely small variations in the voltage against a change of discharge condition.

Therefore, the method is not considered to be a proper measurement for sensing the discharge condition of a battery.

In order to use a method disclosed in EP 119,547, the measurement time or discharge current should increase to enhance the precision of a correlation between the measured value and battery capacity, which obviously reduces the efficiency of measurement.

For a close correlation with battery capacity, it is very important to measure battery characteristics related to physical or chemical parameters highly influenced by the charge/discharge condition of battery, such as internal resistance or impedance.

There has already been reported a method of determining remaining capacity of battery or monitoring battery battery charging/discharging state by measuring internal resistance or impedance at a specified frequency or specified frequency range to measure characteristics related to kinetic parameters of battery.

US Patent No. 3,562,634 describes a method for determining the state of charge a secondary battery, especially nickel-cadmium battery, from the measured Faraday

capacitance by using a bridge. According to US Patent No. 3.562.634, the relationship between the internal impedance of battery and the battery capacity substantially depends on the impedance response characteristic of chemical material used as an active material of the battery.

Therefore the specific relationship between the internal impedance of battery and the battery capacity measured at a specified frequency and for a specified kind of battery do not generally apply to determining battery capacity.

U.S. Patent No. 4.678,998 describes a method for examining the charge/discharge condition of battery using a correlation between the remaining capacity and the internal impedance at a specified frequency. This method has been proposed for the users to determine the charge/discharge condition of an automobile battery continuously.

Besides, US Patent No. 4,743,855 describes a method of using two complex impedances separately measured in the lower and higher frequency regions. and US Patent Nos. 5,241,275 and 5,717,336 disclose the use of the linear impedance characteristic in the lower frequency region. However. the related art method using the relationship between battery capacity and impedance at a specified frequency or in a narrow frequency region is hardly excellent in aspects of efficiency of measurement and accuracy of correlation.

Impedance characteristic of battery can be expressed as a simple equivalent circuit composed of several resistors. capacitors and transmission lines. and the value of model parameters of the equivalent circuit can be calculated from the measured impedance spectrum.

Generally. an impedance of a battery having a close correlation with the charge/discharge condition of a battery is observed at a low frequency of several mHz.

so the proposed equivalent circuit model can be reduced to a simple circuit valid in low frequency region.

According to the present invention, values of parameters are determined by measuring a voltage response upon applied current waveform and subsequent fitting of time domain function of proposed equivalent circuit to the data, or alternatively converting the time domain response into frequency domain impedance data and then fitting complex function of equivalent circuit to this data.

A method using pulse signals provides the same model parameters as obtained in an impedance spectrum measurement method to determine equivalent circuit impedance model parameters at low frequencies.

The present invention uses a simple apparatus including a current generator for applying a current waveform, a voltmeter for measuring the output voltage, a control unit of the voltmeter, and an algorithm, as a result of which a similar time is taken in a measurement but more efficiency can be provided than the above-mentioned conventional methods.

Especially, the present invention presents a greatly efficient method and apparatus to be used in a manufacturing of battery products, since when measuring a plurality of batteries at the same time, a charging/discharging device used in measuring battery capacity in a real time can be reused or used after slight modification.

Disclosure of Invention

Accordingly, an object of the present invention is to provide a method of and apparatus for measuring an unknown battery capacity by measuring voltage response upon applied current waveform and determining parameters correlating with battery capacity either directly from voltage response or after its conversion to frequency

dependent impedance, which take less time than the real-time discharge method and is excellent in efficiency and reliability.

To accomplish the objects of the present invention, a method of measuring the impedance spectrum, which is to measure a characteristic impedance spectrum of primary and secondary batteries and determine the battery capacity, includes the steps of : measuring the characteristic impedance spectrum of primary and secondary batteries in a wide frequency range from the lower frequency of several mHz to the higher frequency of several KHz ,by applying a current waveform to the cell under test and converting the time domain response to frequency domain and calculating model parameters by fitting the measured characteristic impedance spectrum to a complex impedance function corresponding to an equivalent circuit with distributed parameters such as resistors, capacitors and transmission lines: and estimating the unknown battery capacity using parameters obtained in step of calculating of model parameter based on correlation between the capacity measured by the real time discharge method and the model parameters obtained in advance.

Alternatively, a method of measuring the a voltage response signal resulting from applied current pulse includes the steps of: measuring a voltage response signal based on a pulse current signal applied to a primary or secondary battery; performing a fitting of the measured voltage response signal to time domain function corresponding to an equivalent circuit composed of model parameters such as resistors, capacitors and transmission lines to determine the model parameter: and determining the unknown battery capacity from the voltage response characteristics based on a correlation between the measured capacity and the model parameters. the correlation of which is preliminary obtained by a real-time discharge method.

The present invention takes a shorter time than a real-time discharge method

and delivers efficiency and reliability in determining model parameters of an equivalent circuit which are in close correlation with the charge/discharge condition of the battery.

It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory and are intended to provide further explanation of the invention as claimed.

Brief Description of Drawings

FIGS. 1a-1c are circuit diagrams of equivalent circuits having model parameters related to the electrochemical reaction of a battery:

FIG. 2 is a graph showing impedance spectrum experimentally measured and fitted to the equivalent circuit valid in low frequency region shown in FIG. 1a;

FIG. 3 is a graph showing the characteristic impedance spectrum measured of lithium ion battery and fit by equivalent circuit model:

FIG. 4 is an equivalent circuit diagram of a transmission line model;

FIG. 5 is a graph showing a measured voltage response curve resulting from an applied current pulse measured on a nickel-metal hydride battery and fit by time domain response function of equivalent circuit valid in low frequency region.

FIG. 6 is a block diagram of a measurement apparatus in accordance with the present invention;

FIG. 7 is a graph showing a correlation between the remaining capacity of a lithium ion battery and selected model parameter:

FIG. 8 is a graph showing a correlation between the discharge capacity of a fully charged lithium ion battery and selected model parameter: obtained from battery in fully changed state:

FIG. 9 is a graph a correlation between the remaining capacity of a lithium ion

battery and impedances at frequencies of 5 mHz and 60 Hz;

FIG. 10 is a graph a correlation between the remaining capacity of a lithium ion battery and the frequency dependence of impedance in the lower frequency region;

FIGS. 11a and 11b are graphs showing a correlation between model parameters and the remaining capacity of a nickel metal hydride battery during discharge;

FIGS. 12a and 12b are graphs showing a correlation between model parameters and the remaining capacity of a lithium ion battery during discharge; and

FIG. 13 is a graph showing a correlation between model parameters and the remaining capacity of a lithium ion battery in a full charged condition.

Best Mode for Carrying out the Invention

Hereinafter, a method of and apparatus for measuring battery capacity according to the present invention will be described with reference to the accompanying drawings.

Model parameters determined in this invention either directly from voltage response or after its conversion into impedance can be considered as follows, which have a correlation with capacity in the electrochemical reaction of an electrode active material related to the charge/discharge condition.

As shown in FIG. 1a, the surface impedance Z_i of substance A adsorbed to the surface of an electrode in an oxidation/reduction reaction $A - e^- = A^+$ can be expressed with a simple equivalent circuit model, which is composed of charge transfer resistance R_{ct}, pseudocapacitance C_{ps}, double layer capacitance C_{dl}, and serial resistance R_{ser} contributed by resistance of electrolyte and wires.

Pseudocapacitance C_{ps} is given by equation 2:

[Equation 2]

$$C_{ps} = \frac{S \cdot F \cdot z}{dE/dc}$$

where S is the surface area of the electrode, F is the Faraday constant, z is the number of migrating charges, and dE/dc is a potential-concentration coefficient.

Using the Nernst equation in Equation 2, we write Equation 3:

[Equation 3]

$$C_{ps} = \frac{F^2 c_0 z}{RT} \cdot \frac{\exp\{\frac{zF}{RT}(E - E_0)\}}{\exp\{\frac{zF}{RT}(E - E_0)\} + 1}$$

where c_0 is the equilibrium concentration of species related to the redox reaction, E is electrochemical potential in the charge/dischage state of battery, E_0 is electrochemical potential in the equilibrium state, R is gas constant and T is temperature, respectively.

The pseudocapacitance C_{ps} is a model parameter related to the amount of redox species. The reaction mechanism may be more complicated in an actual battery because the species are not simply adsorbed to the electrode surface but distributed in the space of a porous electrode material. But, it can be approximated to an electrode adsorption model at a low frequency of several mHz, so that the pseudocapacitance can be obtained from a relationship with the imaginary part of the complex impedance at the low frequency. The relationship can be expressed by:

$$Z'' = -\frac{1}{\omega}C_{ps}$$

where ω is $2\pi f$.

An application of such a model parameter related to the impedance spectrum has been described in detail by C. Ho, I. R. Raistrick, R. A. Huggins, J. Electrochem. Soc. 127, 343 (1980).

As a measurement for the complex impedance, the Fourier transform method is used by applying a perturbation current signal galvanostatically to both terminals of battery to be measured and by Fourier-transforming a recorded voltage response signal in time domain to frequency domain.

The perturbation current signal used as an input signal is generated by superposition of multiple sinusoidal waves corresponding to multiply selected frequencies. If the

lowest frequency is f_{min}, for example, the oscillation current signal can be composed of $3f_{min}$, $5f_{min}$, $7f_{min}$ and the like.

The finite multiple frequency Fourier transform method is different from that using

pulses (US Patent No. 5633801).

The principle of the measurement is disclosed by G. S. Popkirov and R. N. Schindler, Rev. Sci. Instrum., 63, 5366 (1992).

The maximum frequency that can be determined by the Fourier transform impedance

measurement using multiple frequencies is limited by the sampling time of a signal recorder. The perturbation current is applied for two cycles of the lowest frequency and only the second cycle data are used in the analysis in order to avoid transient effect in the lower frequency region.

Compared with a method using frequency response analyzer which employs single frequency perturbation signal, the time required for measuring impedance by Fourier transform reduced by more than about 1/2.

When impedance spectrum is measured by Fourier transform method, it is possible to determine the linearity of the measurement system with respect to the

current applied to the battery by comparing magnitudes of complex voltages at applied frequencies and those detected at unselected frequencies.

This is also an advantage of the Fourier transform impedance measurement, by which the errors of the measurement can be checked and obtained at the same time as the impedance measurement.

Actually, the impedance spectrum of battery measured as a function of frequency usually differs from the case of ideal interfacial adsorption as illustrated in FIG. 2 when it is expressed on a complex plane.

For the typical impedance spectrum (circular part of data) of lithium ion battery shown in FIG. 3, the semicircular spectrum is distorted into the oval form and has an inclination of 45 degrees in the mid-frequency band.

This phenomenon is characteristic of a battery employing porous electrodes and can be modeled with an equivalent circuit consisting of transmission line as described by E. Barsoukov. J. Hyun Kim, J. Hun Kim. C. O. Yoon. H. Lee. J. Electrochem. Soc. (145 (1998) 2711).

As shown in FIG.4. the transmission line model consists of specific resistance of electrode active material ρ and interfacial impedance Zi of electrode in FIG.1a which are equivalent to distributed serial resistance and distributed parallel impedance in the form of transmission line as usual in electronics.

In the transmission line model, the dc approximation R_r to which the specific resistance of electrode active material contributes and prescribed pseudocapacitance C_{ps} can be model parameters having correlation with battery capacity. The parameters of characteristic impedance function obtained from the solution of differential equation of equivalent circuit can be calculated from the measured impedance spectrum by the complex nonlinear least square fitting method.

The complex nonlinear least square fit of lithium ion battery obtained by using the transmission line model is represented by the solid line in FIG. 3.

Thus the fit of impedance spectra provides information concerning the model parameters.

For a certain battery, model parameters having a relation with battery capacity are primarily determined by the impedance characteristic at a low frequency.

In this case, methods in this invention can be simplified to obtain model parameters directly from time domain response.

Generally, response characteristic E(t) of a linear circuit as a function of an input signal I(t) in a given time interval is obtained from a inverse Laplace transform with respect to a product of a transfer function H(s) and the Laplace transform I(s) of the input signal, as expressed by Equation 4:

[Equation 4]

$$E(t) = \mathcal{L}^{-1}\{H(s)I(s)\}$$

For a step-wise current input signal varying from 0 to I_0 in current intensity when t = 0, the Laplace transform is given by

$$I(s) = \frac{I_0}{s}$$

, and the transfer function H(s) is expressed by impedance function Z(s).

If $C_{dl} << C_{ps}$, the impedance function of an equivalent circuit shown in FIG. 1a can be approximated by Equation 5, which determines the impedance function given by the equivalent circuit of FIG. 1b.

[Equation 5]

$$Z(s) = R_{ser} + \frac{1}{sC_{ps}} + \frac{1}{1/R_{ct} + 1/sC_{dl}}$$

On the other hand, the inverse Laplace transform in Equation 4 is defined by the Bromwich integral equation expressed by:

[Equation 6]

$$f(t) = \frac{1}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty} F(s)e^{st}ds$$

The inverse Laplace transform of the integrated function in Equation 6 is realized simply with reference to the Laplace transform table of an analytical function. or through a numerical analysis (see. T. Hosono. 'Fast Inversion of Laplace Transform in BASIC', Kyoritsu Shupan, Tokyo (1984)).

When $C_{dl} << C_{ps}$, the response characteristic of the equivalent circuit shown in FIG. 1a can be calculated by Equation 7 which is rewritten from Equations 5 and 6.

[Equation 7]

$$E(t) = I_0R_{ser} + I_0R_{ct} + \frac{I_0}{C_{ps}}t - I_0R_{ct}\exp(-\frac{t}{C_{dl}R_{ct}})$$

The response voltage characteristic based on a pulse current is expressed by a function having model parameters constituting an equivalent circuit according to Equation 7. Actually. the model parameters can be calculated by fitting the measured response characteristic to the function by way of linear regression or nonlinear least square fitting method.

On the other hand. in a sufficient long time interval (where. time $t >> C_{dl}R_{ct}$). the equivalent circuit expressed by Equation 5 can be approximated to the simpler form as shown in FIG. 1c.

This results in a linear response curve plotting the voltage against the current pulse as shown in FIG. 5.

Here, $R_{Lim} = R_{ser} + R_{ct}$ and $C_{Lim} \fallingdotseq C_{ps}$

The current to be applied to the battery must be in a range of intensity such that the internal resistance causes a voltage drop not larger than 200mV, preferably not larger than 50mV.

The pulse has to be selected to have a length that the voltage signal can be approximated to have linearity.

FIG. 6 is a block diagram of a unit for measuring battery capacity by applying to a test battery a perturbation current signal generated by superposition of non overlapping multiple frequencies or a defined pulse current. and measuring the current and voltage response signals of the battery based on the applied perturbation current signal or defined pulse current.

Here, reference number 10 is a control means for controlling to apply to a test battery the perturbation current signal generated by superposition of non overlapping multiple frequencies or the defined pulse current, and measuring the capacity of the test battery 30 by inputting the current and voltage response signals of the test battery 30 based on the applied perturbation current signal and defined pulse current.

The control means 10 includes: a control/arithmetic unit 11 for controlling the apply of the perturbation current signal generated by superposition of non-overlapping multiple frequencies or a defined pulse current to a test battery 30. and controlling the measurement of the capacity of test battery 30 with the current and voltage response signals of the test battery 30 according to the applied perturbation current signal and defined pulse current: a memory 13 for storing and outputting the current and voltage response signals of the test battery 30 inputted; an input/output(I/O) unit 15 for

outputting the perturbation current signal of the control/arithmetic unit 11 or the apply control command of the defined pulse current, and inputting the measured current and voltage response signals of the test battery 30, and thereby applying them to the memory 13; an impedance spectrum measuring means 17 for Fourier-transforming the current and voltage response signals of the test battery 30 stored in the memory 13 according to the control of the control/arithmetic unit 11 and approximating to a value of characteristic factor; and a pulse current measuring means 19 for approximating the current and voltage response signals of the test battery 30 stored in the memory 13 to a value of characteristic factor according to the control of the control/arithmetic unit 11.

Reference number 20 denotes a measuring means for applying to the test battery the perturbation current signal generated by superposition of non-overlapping multiple frequencies or a defined pulse current according to the control of the control means 10, and measuring the current and voltage response signals of the test battery based on the applied perturbation current signal and defined pulse current, thus inputting them to the control means 10.

The measuring means 20 includes: a signal generating unit 21 for generating a perturbation current signal generated by superposition of non-overlapping multiple frequencies or a defined pulse current according to the control of the control means 10 on order to apply them to the test battery 30; a constant current control unit 23 for applying the perturbation current signal and the defined pulse current output from the signal generating unit 21 to the test battery 30, and defined pulse current and outputting voltage response signal V_{out} and current response signal I_{out} of the test battery 30 based on the applied perturbation current signal and the defined pulse current; first and second filters 25 and 25A for filtering each of the voltage response signal V_{out} and current response signal I_{out} output from the constant current control unit 23 and removing noise

out of them; first and second amplifiers 27 and 27A for amplifying the output signals of the first and second filters 25 and 25A; and a two-channel analog/digital(A/D) converter 29 for converting an output signal of the first and second amplifiers 27 and 27A into digital signal and inputting it to the control means 10.

The measuring means 20 has multi-channels. Therefore, a plurality of measuring means are connected to one control means 10. thereby individually measuring the capacity of the test battery 30 simultaneously.

In the thus-structured measuring means. when the measuring method is selected and a capacity is measured by connecting the measuring means to the test battery 30. the control/arithmetic means 11 of the control means 10 generates a control command. which is then input to a signal generating unit 21 of the measuring means 20 through the input/output unit 15.

The signal generating unit 21 stores/outputs a perturbation current signal I_{in} made by superposition of non-overlapping multiple frequency in case it measures an impedance of the test battery 30 by generating an input current signal I_{in} supposed to be input to the test battery 30 according to the control command. and stores/outputs a pulse current signal I_{in} with a defined length and size in case of measuring in a pulse current measuring method.

According to the current signal I_{in} output from the signal generating unit 21. the constant current control unit 23 generates constant current. followed by applying it to the test battery 30 and outputs a voltage response signal V_{out} and a current response signal I_{out} of the test battery 30 based on the constant current of the input current signal I_{in} applied.

The voltage and current response signals V_{out} and I_{out} output from the constant current control unit 23 are filtered in the first and second filters 25 and 25A individually

in order to remove noise. amplified in the first and second amplifiers 27 and 27A, and converted into the digital signal in the analog/digital(A/D) converter 29.

The digital signal from the analog/digital(A/D) converter 29 is input to the input/output unit(I/O) 15 of the control means 10 and stored in the memory 13.

Here, if the capacity of the test battery 30 is measured in the pulse current measuring method, the current response signal I_{out} is not used, and there is no need to convert it into the digital signal.

In this state, the control means 10 approximates the measuring result stored in the memory 13. namely, the voltage and current response signals V_{out} and I_{out} to the value of the characteristic factor.

For example, in case of an impedance spectrum measurement. the impedance spectrum measuring means 17 Fourier-transforms the digital signal of the voltage and current response signals V_{out} and I_{out} stored in the memory 13. namely, the impedance spectrum into a complex impedance value denoted by function of frequency. and then approximates the complex impedance value to a value of the characteristic factor predefined according to the function fitting algorithm. And in case of using the pulse current measuring method. the pulse current measuring means 19 fits the voltage response signal V_{out} into the value of characteristic factor pre-defined according to the response voltage function fitting algorithm.

If fitted into the predefined value of characteristic factor, is firstly examined the correlation between the value of the fitted characteristic factor and the capacity of battery measured in the real-time discharge method. and then determines the capacity of battery from the measured parameters characteristic factor of the battery of a unknown capacity based on the correlation.

Here. when simultaneously measuring a plurality of test batteries 30 in a multi-

channel method. the control means 10 performs a successive calculation corresponding to the function fitting or a nonlinear fitting into the response voltage function, and the calculation arithmetical time, however, can be ignored in comparison to the time for measuring the input and output signal.

Further, it is possible to realize a very effective apparatus for measuring and grading battery capacity by incorporating the standard battery products with a measurement unit of the present invention and a general charge/discharge equipment for controlling the charge/discharge condition in real time.

Embodiment 1 (Comparative Example)

A Fourier transform impedance spectrometer is manufactured which is designed to

apply an input current signal having superposition of multiple sine waves obtained by superposing odd-numbered times of the lowest frequency to a battery via a 16-bit D/A converter and a galvanostat, and transfer digital current and voltage signals measured by a two-channel 16-bit A/D converter to a computer for calculating a complex impedance by use of the digital discrete Fast Fourier transform algorithm. Herein, the pulse current measurement unit is used by storing the pulse input signal to a 16-bit A/D converter.

Table 1 lists the required times in different measurements of the capacity of a charged battery. In this embodiment. there are used a real-time discharging method; a frequency scanning method which is performed by the number of selected frequencies at constant intervals in the range of 5 mHz to 20 kHz. e.g.. 20. 40 and 60 frequencies: an impedance spectrum measuring method using a minimum sine wave of 5 mHz frequency: and a pulse current measuring method with a pulse signal.

Table 1 : Comparison of required times in measurement of the battery capacity.

A	B	C	D	Ref.
> 1 hour	363 sec	200 sec	100 sec	20
	620 sec			40
	880 sec			60

Note. A : real-time discharging method

B : frequency scanning method

C : impedance spectrum measuring method

D : pulse current measuring method

As shown in Table 1, a use of the impedance spectrum measuring method and pulse current measuring method of the remaining capacity of a battery provide a reduction in the required time than the frequency scanning method..

Embodiment 2

A lithium ion battery (manufactured by Sony Co.) with regulated capacity of 1300 mAh is charged up to 4.2 volts under condition of constant current for one hour at room temperature and fully charged at the voltage for 2.5 hours under condition of constant voltage. Then use is made of a Fourier transform impedance meter as described in embodiment 1 in measuring the impedance spectrum in the frequency range from 5 mHz to 20 KHz.

To obtain the impedance spectrum of the same battery in different discharge states, the battery is repeatedly discharged by 130 mAh under condition of constant current for 10 hours and the impedance spectra are measured successively.

The impedance spectra are fitted by the complex nonlinear least square fitting

method for the impedance function corresponding to the transmission line equivalent circuit model shown in FIG. 4 to calculate a model parameter, pseudocapacitance C_{ps}. A comparison of the model parameter and remaining capacity in each discharge state measured by the real-time discharge method at constant current for 5 hours reveals that there is a close correlation between the model parameter and the remaining capacity, as shown in FIG. 7.

The time required for measuring the impedance spectrum in each discharge state and calculating the model parameter by fitting did not exceed 420 seconds.

Embodiment 3

Lithium ion batteries with nominal capacity of 1300 mAh with unknown user history

are fully charged in the same manner as embodiment 2. Then impedance spectum is measured to calculate a model parameter, charge transfer resistance R_{ct}.

These batteries are discharged down to the final voltage of 2.7 V at a constant current of five-hour rate at room temperature and the discharge capacity of each battery is calculated. A comparison of the discharge capacity shows a correlation between the model parameter and the discharge capacity, as illustrated in FIG. 8.

The time required for measuring the impedance spectrum for each battery and calculating the model parameter by approximation did not exceed 420 seconds.

Embodiment 4 (Comparative Example)

A comparison of the remaining capacity of battery and impedance at specified frequencies (5 mHz, 60 Hz) instead of model parameter for the impedance spectrum measured in embodiment 2 reveals that there is no close correlation between the impedance at each frequency and the remaining capacity, as shown in FIG.9.

Embodiment 5 (Comparative Example)

To compare the remaining capacity of battery and the numerical value derived from the frequency dependence of real or imaginary part of the internal impedance of battery, obtained or extrapolated from relatively narrow frequency range, instead of calculating model parameters for the impedance spectrum measured in embodiment 2, the relationship is examined between the imaginary value of impedance in the lower frequency region and the square root of the frequency. As a result, no close correlation is found between the absolute value and the remaining capacity, as illustrated in FIG. 10.

Embodiment 6

At a six-hour charge rate under constant current and room temperature condition, a nickel metal hydride battery (manufactured by Emmerich) having a nominal capacity of 600 mAh is and discharge and stabilized for about 10 minutes. During an application of +30 mA current (charging current) and -30 mA current (discharging current) each for 100 seconds to the nickel metal hydride battery, the voltage is measured as a function of time.

The intensity of the current pulse, 30 mA is determined in the range that maintains the linearity of the voltage response.

Low-frequency limiting resistance R_{Lim}, and low-frequency limiting capacitance C_{Lim} which are model parameters of the equivalent circuit of FIG. 1a are calculated from the slope and y-intercept of the linear line obtained through a linear regression from the voltage response characteristic based on charge current.

In order to obtain the pulse current response characteristic in another discharge condition of the same battery, the nickel metal hydride battery is discharged each time by 30 mAh at a 60 mA constant current condition and repeatedly measured in regards to the pulse current in an analogous manner as described above. Subsequently, model

parameters such as low-frequency limiting resistance R_{Lim}, and low-frequency limiting capacitance C_{Lim} are calculated.

As apparent from table 1 and FIGS. 11a and 11b, a comparison of the remaining capacities of the battery which are measured in each discharge condition by a real-time discharge method at a 60 mA constant current condition reveals that there is a close correlation between the remaining capacity and the model parameters, i.e., low-frequency limiting capacitance and low-frequency limiting resistance.

Embodiment 7

A lithium ion battery (manufactured by Sony) having a nominal capacity of 1300 mAh is charged to 4.2 volts at the 1-hour rate in a constant current for one hour and room temperature condition, and stabilized for 2.5 hours under a 4.2 V constant voltage condition. After this, a voltage response curve of the battery is obtained after performing the same current pulse measurement unit as described in embodiment 6.

In order to obtain a response curve of the identical battery in another discharge state, the battery is discharged each time by 60 mAh in a 120 mA constant current condition and repeatedly measured in regards to the pulse current.

The used pulse current is +100 mA in intensity and has a time width of 400 seconds.

For each voltage response curve, model parameters such as low-frequency limiting resistance R_{Lim}, and low-frequency limiting capacitance C_{Lim} are calculated through a linear regression of an impedance function corresponding to the equivalent circuit of FIG. 1c. As shown in FIGS. 12a and 12b, a comparison of the remaining capacities of the battery which are measured in each discharge condition by a real-time discharge method using a constant current of 120 mA reveals that there is a close correlation between the remaining capacity and the model parameters, i.e., low-

frequency limiting capacitance and low-frequency limiting resistance.

The time required to measure the voltage response curve and obtain model parameters through a fitting in each discharge condition did not exceed 200 seconds.

Embodiment 8

Six lithium ion batteries (manufactured by Sanyo) each of which has a nominal capacity of 1300 mAh and unknown history are charged. and a voltage response curve of each battery is obtained with the current pulse used in embodiment 7.

Model parameters are calculated by the non-linear least square fitting method according to Equation 7.

The batteries are discharged to a 2.7 volts at the 5-hour rate in a constant current and room temperature condition, and the discharge capacity of each battery for a measured discharge period is calculated. As apparent from table 2 and FIG. 13, there is a close correlation between the remaining capacity and the model parameters, i.e., low-frequency limiting capacitance C_{dl} and low-frequency limiting resistance C_{ps}.

The time required to measure the voltage response curve and obtain model parameters through an approximation did not exceed 200 seconds.

Table 2 : Results of an analysis for the electrical capacity and the response signals based on the pulse current of each lithium ion battery obtained through a real-time discharge method.

CAPACITY (mAh)	R_{ct} (Ω)	C_{dl} (Farad)	C_{ps} (Farad)
1463	0.1939	14.67	1230.9
1409	0.1830	19.01	1174.9
1331	0.2352	25.89	1105.8
1189	0.2848	26.27	1045.8

1145	0.4595	28.52	1032.8
992	0.4619	28.60	973.1

Industrial Application

Such as in the present invention described above, there is provided with a measurement of a unknown battery capacity by measuring parameters obtained from voltage response signal of a current waveform or impedance spectrum generated thereof, is more excellent in efficiency and accuracy than the related art measurement for battery capacity. Such a measurement can be used for the user to measure the capacity of primary and secondary batteries used for portable electronics, power tools, communication equipment, automobiles and electric vehicles, or to measure or grade the battery capacity in production of the primary and secondary batteries on a large scale.

It will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the spirit or scope of the invention. Thus, it is intended that the present invention cover the modifications and variations of this invention provided they come within the scope of the appended claims and their equivalents.

WHAT IS CLAIMED IS

1. A method of measuring battery capacity using a voltage or current response signal resulting from applied current or voltage waveform, comprising the steps of:,

(1) measuring a voltage or current response signal resulting from current or voltage excitation signal applied to the both ends of the battery as a function of time;

(2) analyzing the measured signal to determine parameter or parameters of predefined impedance model of battery;

(3) examining a correlation between parameter or parameters and the capacity of the battery measured by a real-time discharge method; and

(4) based on the correlation, determining the unknown capacity of the battery from parameter or parameters obtained from the response to the excitation signal applied to the battery with unknown capacity based on the correlation.

2. The method as defined in claim 1, wherein the intensity of the excitation signal less than one necessary to fully discharge battery in 1 hr time, calculated based on rated battery capacity.

3. The method as defined in claim 1, wherein a required time in second to measure the voltage characteristic in response to the excitation signal is below 1/10 of full discharge time at given current or voltage calculated from rated battery capacity.

4. A method of measuring battery capacity as described in claim 1, where applied waveform is a current or voltage pulse, comprising the steps of:

(1) measuring a response signal resulting from on a pulse current or voltage excitation signal applied to the both ends of the battery as a function of time;

(2) analyzing the measured response signal to determine impedance model parameter or parameters;

(3) examining a correlation between the parameter or parameters and the capacity of the battery measured by a real-time discharge method;

(4) determining the unknown capacity of the battery form parameters or parameters obtained from a response signal to the pulse excitation applied to the battery based on the correlation.

5. The method as defined in claim 4, wherein the intensity of the excitation signal is less than one necessary to fully discharge battery in 1 hr time, calculated based on rated battery capacity.

6. The method as defined in claim 4. wherein a required time in second to measure the response signal to the pulse excitation is below 1/10 of full discharge time at given current calculated from rated battery capacity.

7. The method as defined in claim 4. wherein the parameters are model parameters determined from an fitting of the measured response signal to a time domain response function obtained from an equivalent circuit comprising resistors, capacitors or transmission lines.

8. The method as defined in claim 4. wherein analyzing the measured response signal is performed by fitting to a response function obtained by inverse Laplace's transform of the inpedance function of model circuit multiplied by current pulse function expressed in Laplace domain or divided by voltage pulse function

expressed in Laplace domain.

9. A method of measuring battery capacity as in claim 1, where response from applied waveform is transformed to complex impedance spectrum prior to analysis, the method comprising the steps of:

(1) measuring a voltage or current response signal resulting from an current or voltage excitation waveform applied to the both ends of the battery as a function of time;

(2) conversion of obtained response waveform into impedance specturm of a battery in a predetermined frequency region;

(3) determining one or more parameter from the measured impedance spectrum;

(4) monitoring in advance the correlation between the determined model parameter or parameters and the battery capacity measured by a real-time discharge technique; and

(5) determining the battery capacity from parameter or parameters obtained from the characteristic impedance spectrum of a battery having an unknown capacity based on the correlation.

10. The method as claimed in claim 9, wherein the predetermined frequency region has the ratio of the highest and lowest frequencies is at least 100.

11. The method as claimed in claim 9, wherein the parameters are model parameters determined by fitting the measured impedance spectrum to an impedance function of an equivalent circuit comprising resistors, capacitors and transmission lines.

12. The method as claimed in claim 9, wherein the input signal is applied to both terminals of battery under galvanostatic conditions.

13. The method as claimed in claim 9, wherein the required time for application of current perturbation in measurement of impedance spectrum for once is within 1 hour.

14. The method as claimed in claim 9. a complex nonlinear least square fitting of impedance data to the impedance function of the model circuit is used to obtain the parameters of model circuit.

15. The method as claimed in claim 9. where the applied excitation waveform is a combination of not overlapping sine-waves having selected frequencies which waveform can be transformed into frequency domain so that ratio between the amplitudes of selected frequencies to amplitudes of other frequencies is more then 100.

16. The method as claimed in claim 9, where fast Fourier transform is used to obtain impedance spectra from the measured response signal.

17. The method as claimed in claim 9, where the applied waveform is a current or voltage pulse and Laplace transform is used to obtain impedance spectrum from measured response signal.

18. An apparatus for measuring battery capacity, comprising:

a control means to generate a perturbation signal made by an overlap of a non-interference sine waves with selected frequencies or pulse signal and transferring

generated excitation waveform as control signal to measuring means which apply it to battery, further receive detected by measuring means time-varying response signal, analyze it to obtain parameters and determine capacity of the battery

a measuring means for applying the generated in control means perturbation waveform signal consisting of non-interference selected frequencies or a defined pulse signal to a test battery and detecting the time-varying current and voltage response signals of the test battery resulting from the applied perturbation current signal or defined pulse signal, further transmitting it to control means.

19. The apparatus as defined in claim 18, wherein the control means comprises:

a control/arithmetic unit for controlling the apply of the perturbation current signal generated by overlaps of non-interference selective frequency or a defined pulse current to the test battery, and controlling the measurement of the capacity of the test battery with the current and voltage response signals of the test battery based on the applied perturbation current signal and defined pulse current;

a memory for storing and outputting the current and voltage response signals of the test battery inputted;

an input/output unit for outputting the perturbation current signal of the control/arithmetic unit or the apply control command of the defined pulse current, and inputting the current and voltage response signals measured on the test battery, thus storing them into memory;

a model parameter measuring means for fitting the current and voltage response voltage or current signals of the test battery stored in the memory to time-domain function of model circuit to determine values of characteristic factors.

19. The apparatus as defined in claim 18, wherein the control means comprises:

a control/arithmetic unit for controlling the apply of the perturbation current signal generated by overlaps of non-interference selective frequency or a defined pulse current to the test battery, and controlling the measurement of the capacity of the test battery with the current and voltage response signals of the test battery based on the applied perturbation current signal and defined pulse current;

a memory for storing and outputting the current and voltage response signals of the test battery inputted;

an input/output unit for outputting the perturbation current signal of the control/arithmetic unit or the apply control command of the defined pulse current, and inputting the current and voltage response signals measured on the test battery, thus storing them into memory;

a model parameter measuring means including an impedance spectrum measuring means for Fourier-transforming the current and voltage response signals of the test battery stored in the memory and then fitting obtained impedance spectrum to a complex impedance function of model circuit to determine values of characteristic factors.

20. The apparatus as defined in claim 18, wherein the control means has a plurality of measuring means each connected to a battery respectively through multi-channels to thereby receive the perturbation current signal or the defined pulse current, individually detect the voltage and current response signals based on the current applied and input them to an individual control means.

21. The apparatus as defined in claim 18 or 19, wherein the measuring means comprises:

a signal generating unit for storing a pre-defined perturbation input signal and defined pulse current and outputting the perturbation input signal and the defined pulse current selected by the control means;

a constant current control unit for applying the output current of the signal generator to the battery and detecting the current and voltage response signals based on the current applied; and

an analog/digital converter for successively converting the current and voltage response signals detected in the constant current detecting unit into digital signals and inputting them to the control means.

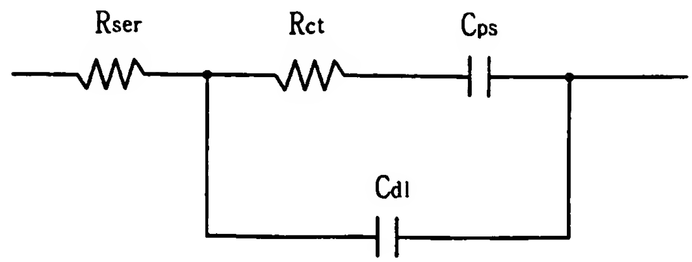
22. The apparatus as defined in claim 15, further comprising:

the first and second filters for respectively filtering the current and voltage response signals detected by the constant current detecting unit to thereby remove noise; and

the first and second amplifiers for amplifying output signal of the first and second filters and inputting them to the analog/digital converter.

FIG. 1

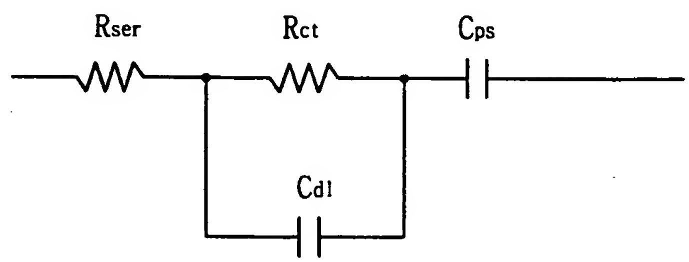
(a)



$$Z(s) = R_{ser} + \cfrac{1}{\cfrac{1}{R_{ct} + \cfrac{1}{sC_{ps}}} + sC_{dl}}$$

$C_{dl} \ll C_{ps}$

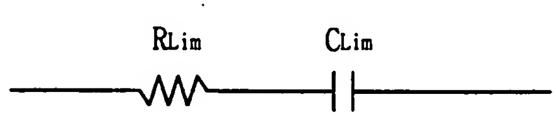
(b)



$$Z(s) = R_{ser} + \cfrac{1}{\cfrac{1}{R_{ct}} + sC_{dl}} + \frac{1}{sC_{ps}}$$

$t \gg C_{dl}R_{ct}$

(c)



$$Z(s) = R_{Lim} + \frac{1}{sC_{Lim}}$$

FIG. 2

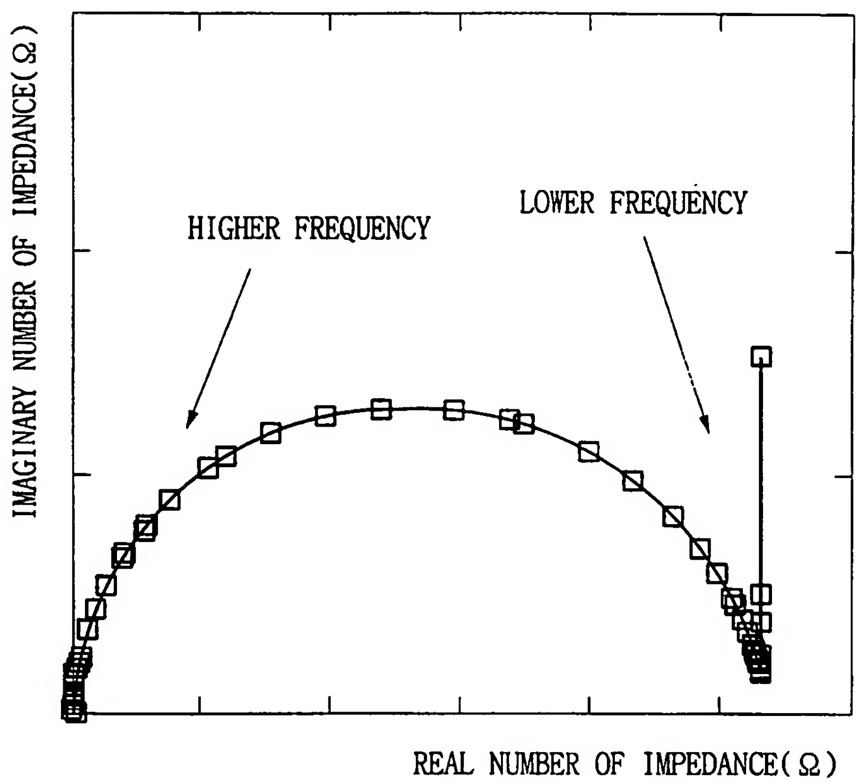

IMAGINARY NUMBER OF IMPEDANCE(Ω)
HIGHER FREQUENCY
LOWER FREQUENCY
REAL NUMBER OF IMPEDANCE(Ω)

FIG. 3

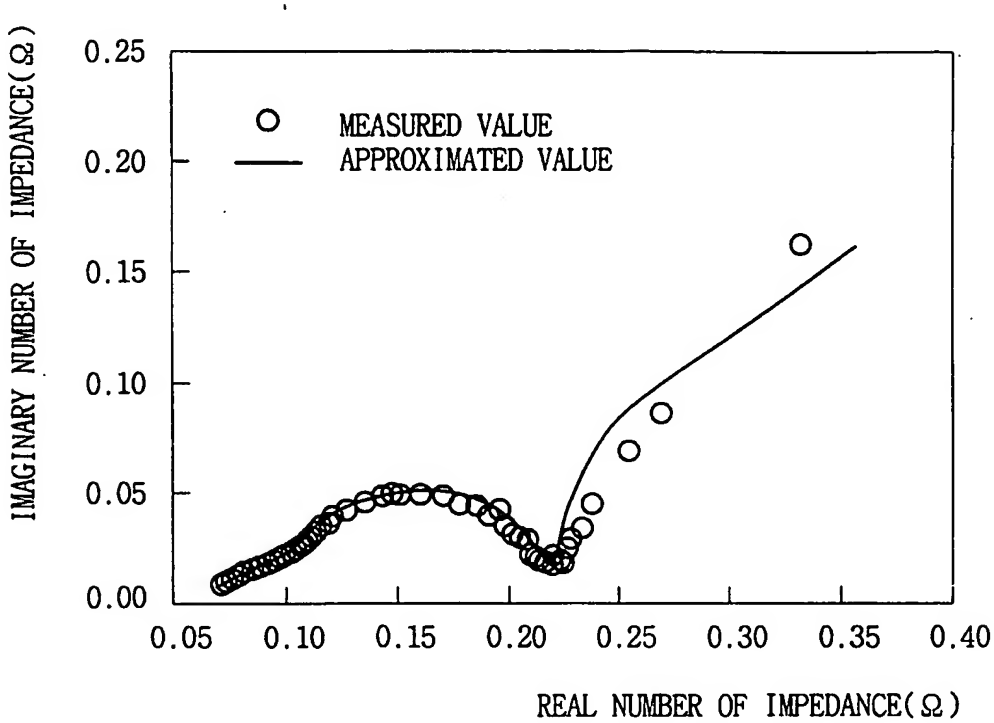

IMAGINARY NUMBER OF IMPEDANCE(Ω)
0.25
0.20
0.15
0.10
0.05
0.00
MEASURED VALUE
APPROXIMATED VALUE
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
REAL NUMBER OF IMPEDANCE(Ω)

FIG. 4

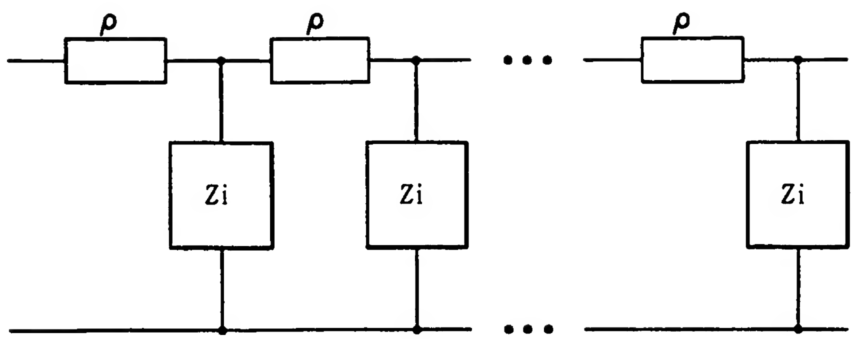

ρ
ρ
ρ
Zi
Zi
Zi

FIG. 5

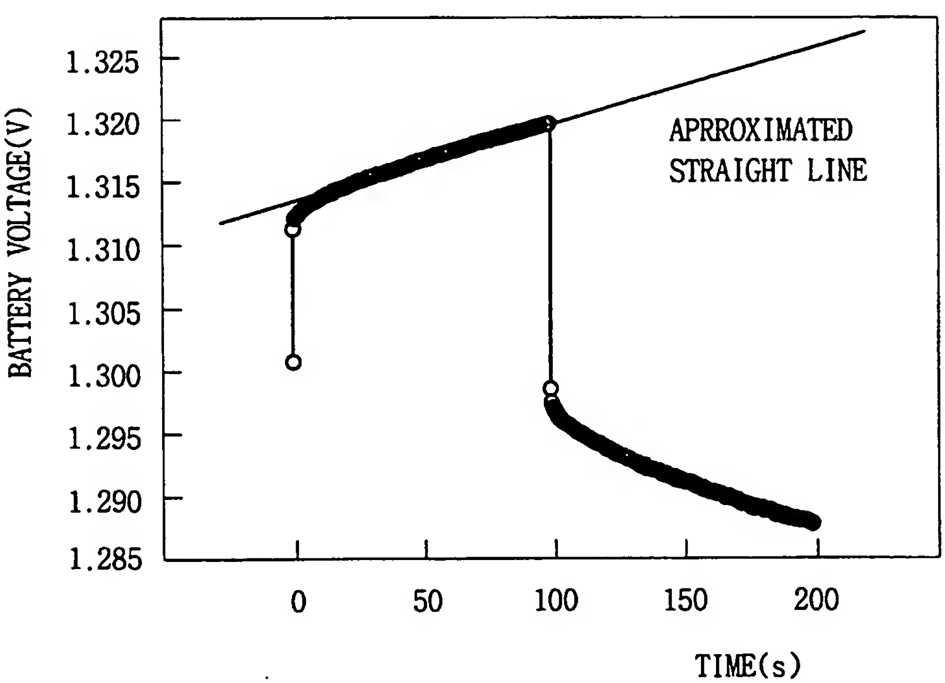

BATTERY VOLTAGE(V)
1.325
1.320
1.315
1.310
1.305
1.300
1.295
1.290
1.285
0
50
100
150
200
TIME(s)
APRROXIMATED
STRAIGHT LINE

FIG. 6

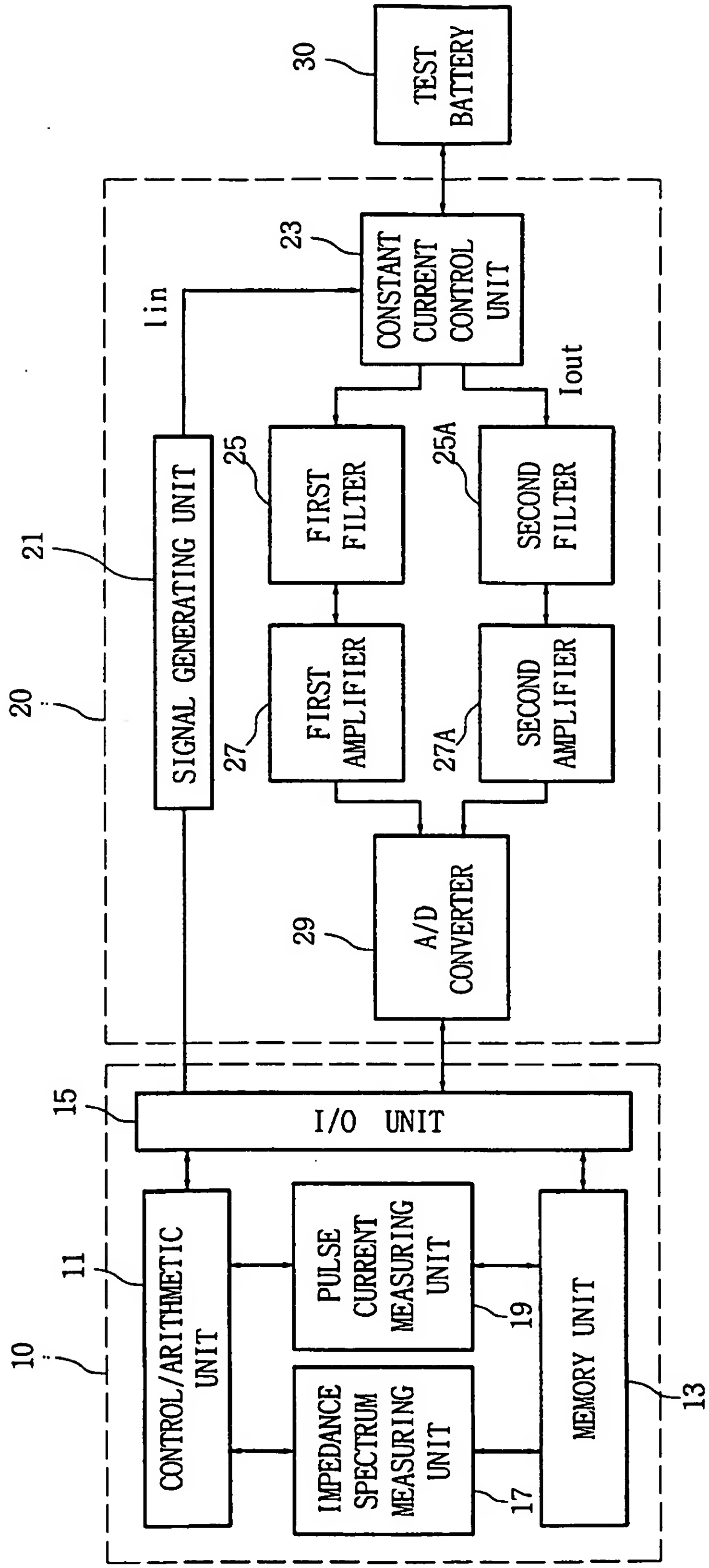

TEST BATTERY
30
CONSTANT CURRENT CONTROL UNIT
23
Iin
Iout
SIGNAL GENERATING UNIT
21
20
FIRST FILTER
25
SECOND FILTER
25A
FIRST AMPLIFIER
27
SECOND AMPLIFIER
27A
A/D CONVERTER
29
I/O UNIT
15
CONTROL/ARITHMETIC UNIT
11
10
PULSE CURRENT MEASURING UNIT
19
IMPEDANCE SPECTRUM MEASURING UNIT
17
MEMORY UNIT
13

FIG. 7

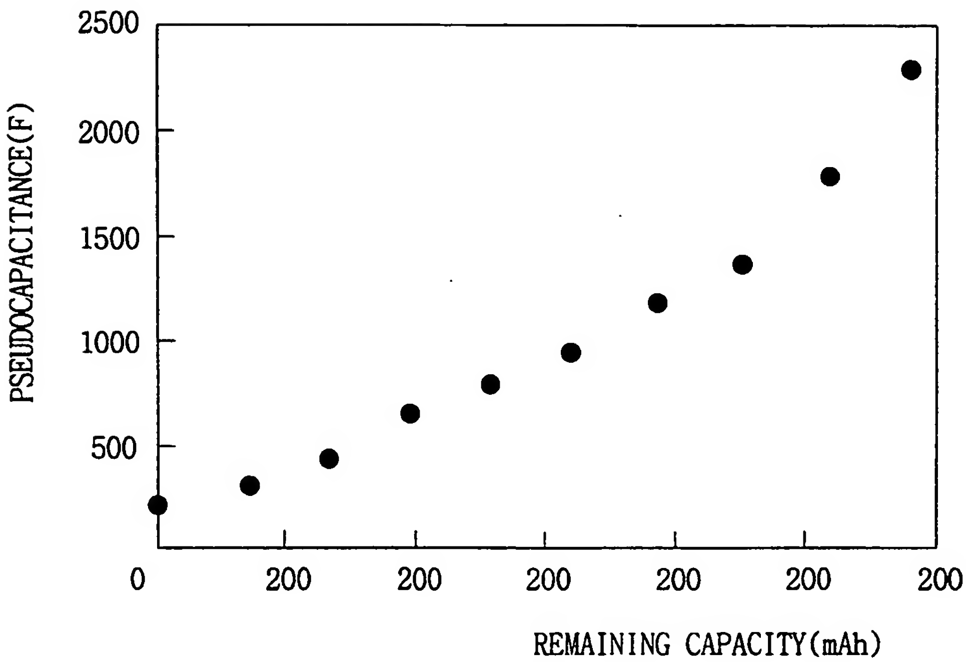

2500
2000
1500
1000
500
PSEUDOCAPACITANCE(F)
0
200
200
200
200
200
200
REMAINING CAPACITY(mAh)

FIG. 8

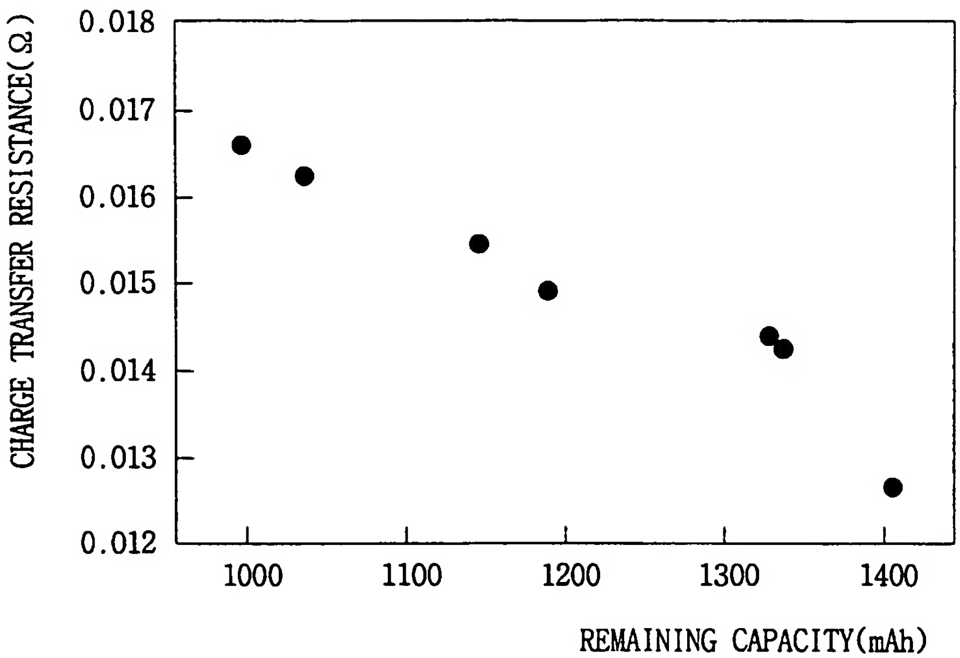

CHARGE TRANSFER RESISTANCE(Ω)
0.018
0.017
0.016
0.015
0.014
0.013
0.012
1000
1100
1200
1300
1400
REMAINING CAPACITY(mAh)

FIG. 9

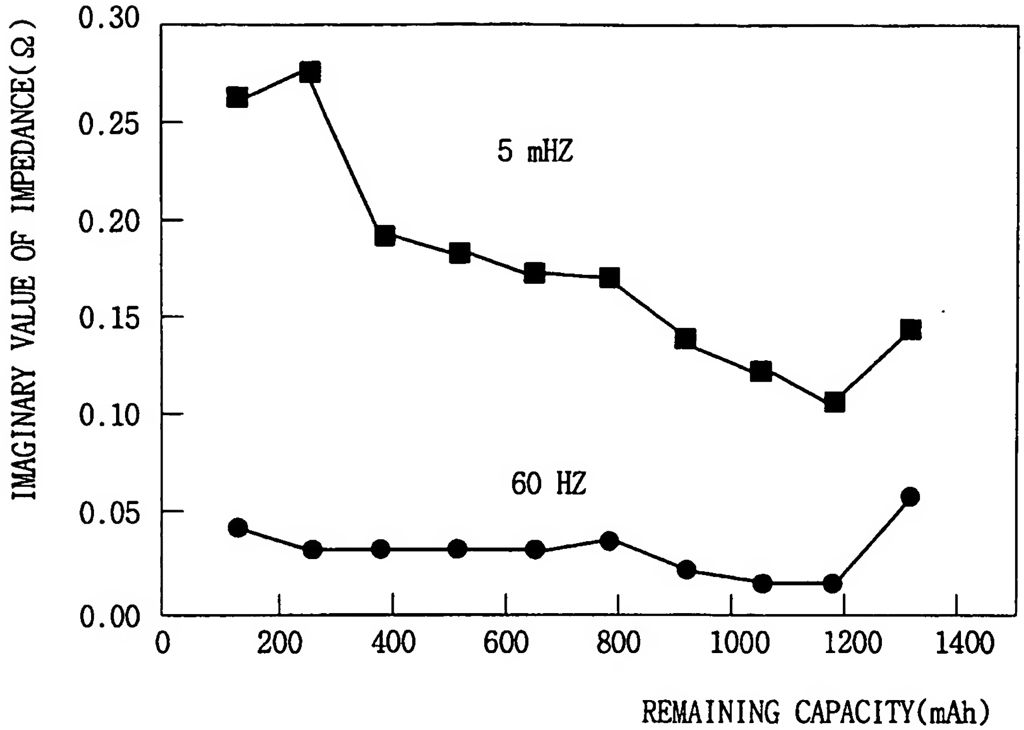
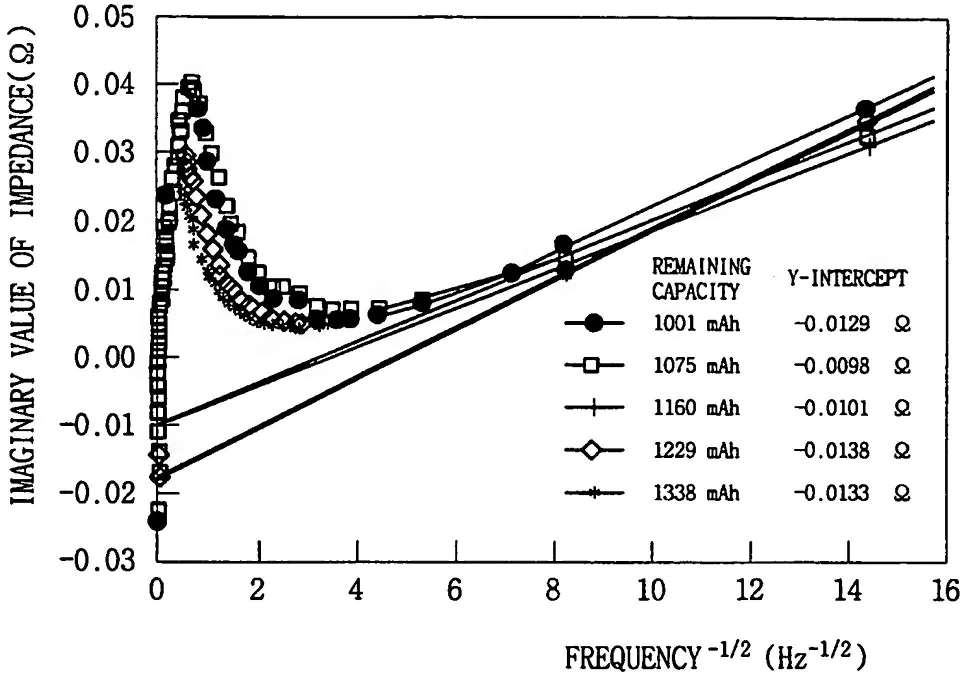

IMAGINARY VALUE OF IMPEDANCE(Ω)
0.30
0.25
0.20
0.15
0.10
0.05
0.00
5 mHZ
60 HZ
0
200
400
600
800
1000
1200
1400
REMAINING CAPACITY(mAh)

FIG. 10



IMAGINARY VALUE OF IMPEDANCE(Ω)
0.05
0.04
0.03
0.02
0.01
0.00
-0.01
-0.02
-0.03
0
2
4
6
8
10
12
14
16
FREQUENCY $^{-1/2}$ (Hz$^{-1/2}$)
REMAINING CAPACITY
Y-INTERCEPT
1001 mAh -0.0129 Ω
1075 mAh -0.0098 Ω
1160 mAh -0.0101 Ω
1229 mAh -0.0138 Ω
1338 mAh -0.0133 Ω

FIG. 11a

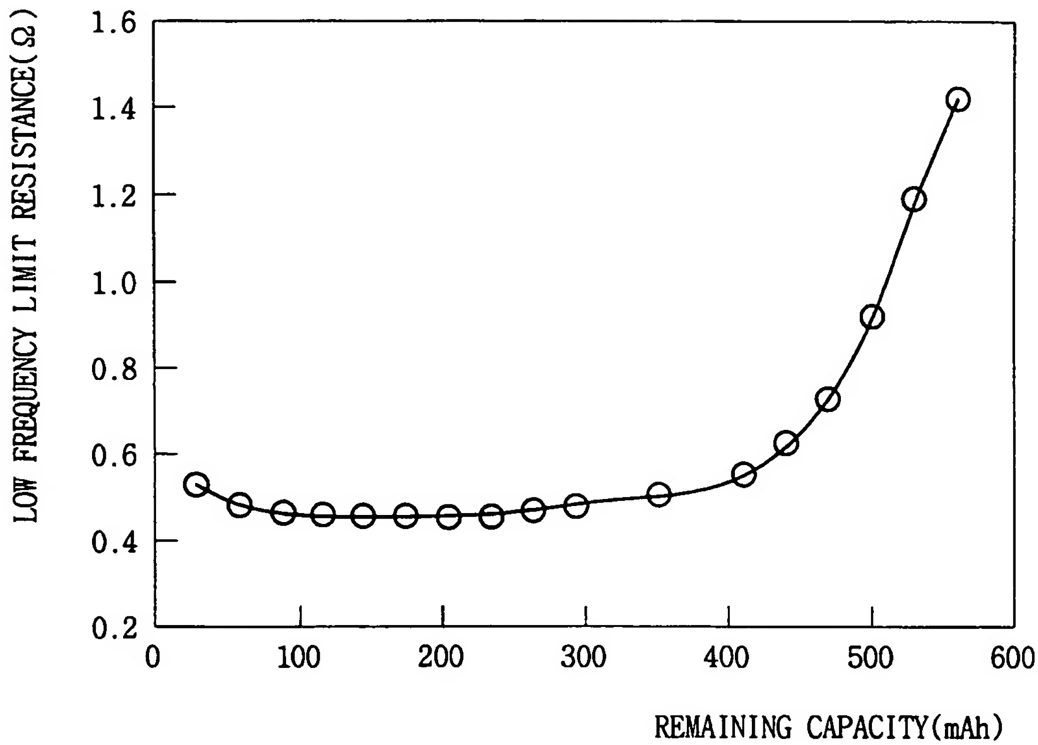

LOW FREQUENCY LIMIT RESISTANCE(Ω)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
100
200
300
400
500
600
REMAINING CAPACITY(mAh)

FIG. 11b

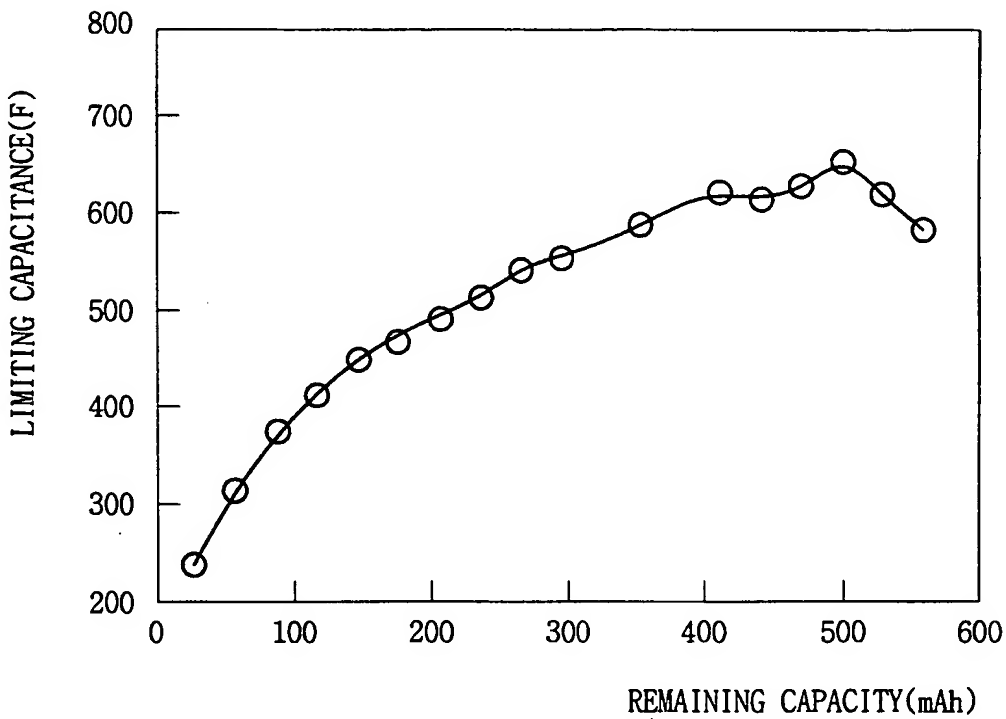

800
700
600
500
400
300
200
0
100
200
300
400
500
600
LIMITING CAPACITANCE(F)
REMAINING CAPACITY(mAh)

FIG. 12a

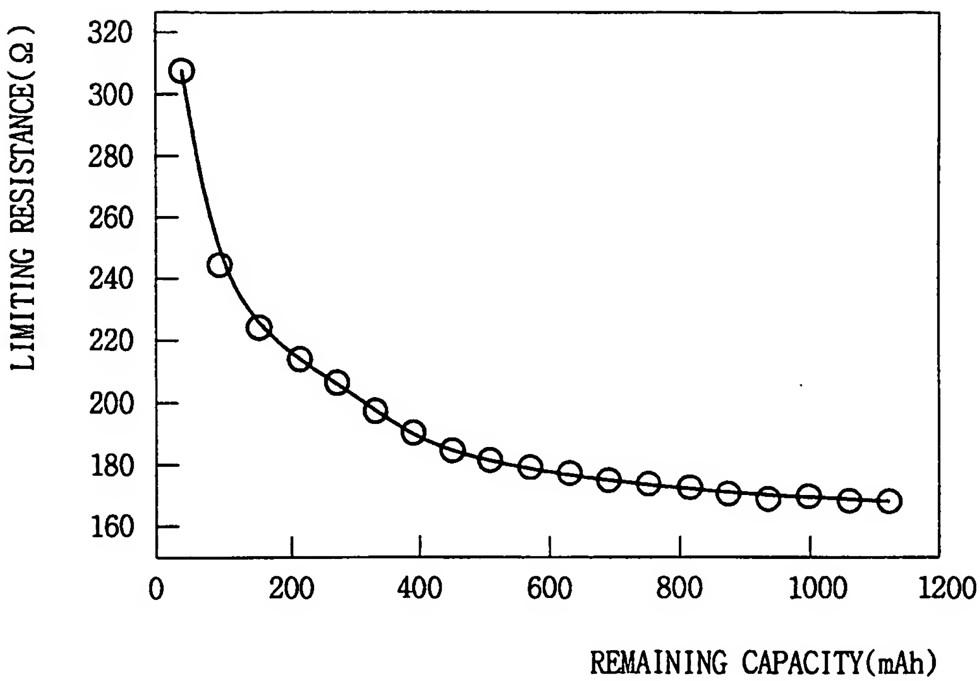

LIMITING RESISTANCE(Ω)
320
300
280
260
240
220
200
180
160
0
200
400
600
800
1000
1200
REMAINING CAPACITY(mAh)

FIG. 12b

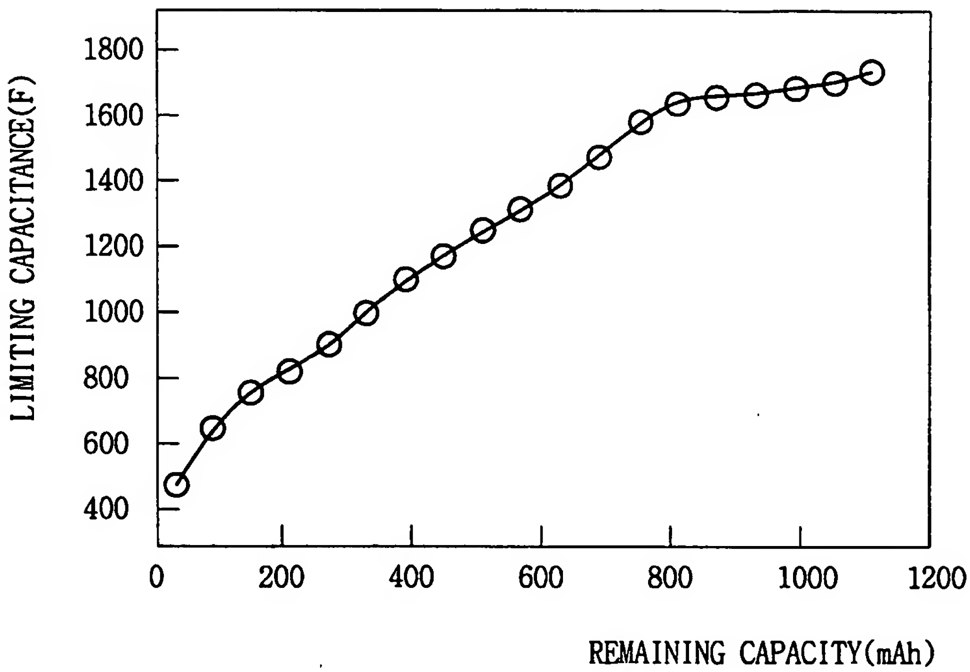
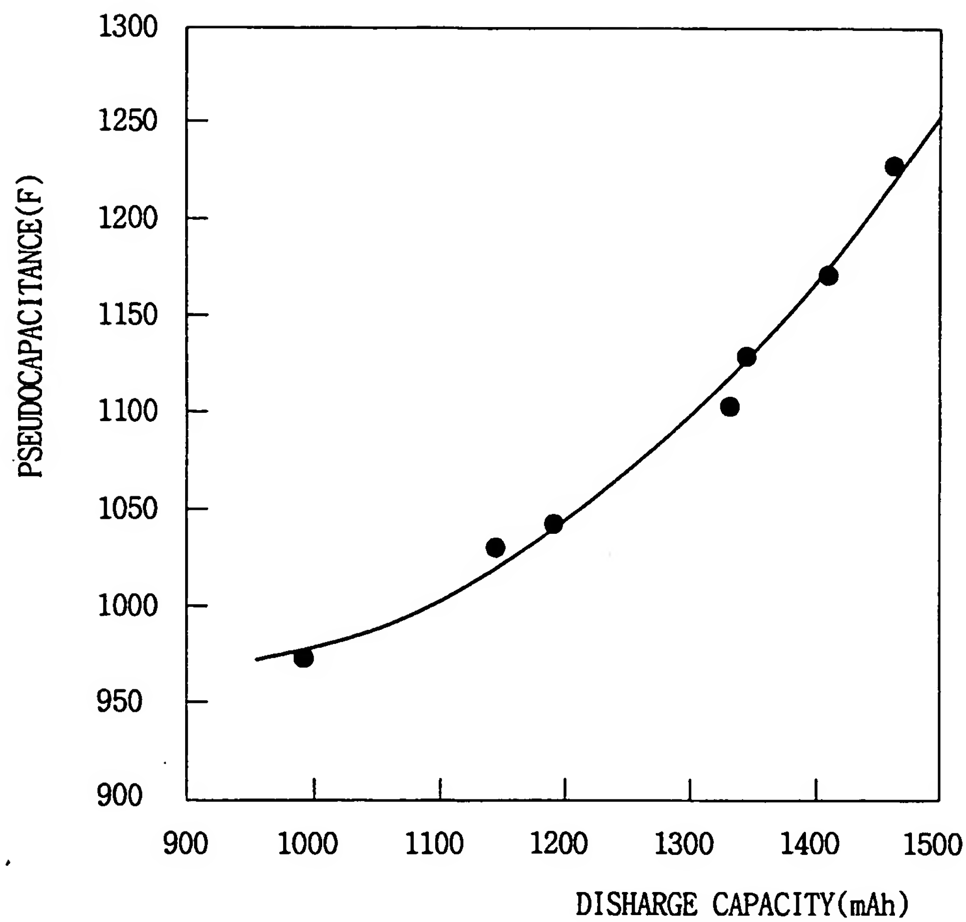

1800
1600
1400
1200
1000
800
600
400
LIMITING CAPACITANCE(F)
0
200
400
600
800
1000
1200
REMAINING CAPACITY(mAh)

FIG. 13


1300
1250
1200
1150
1100
1050
1000
950
900
PSEUDOCAPACITANCE(F)
900
1000
1100
1200
1300
1400
1500
DISHARGE CAPACITY(mAh)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR 99/00304

A. CLASSIFICATION OF SUBJECT MATTER

IPC^6: G 01 R 31/36, 19/165

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC^6: G 01 R 19/00, 31/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 06-337 284 A (OMRON CORP); (abstract), 28 April 1995 (28.04.95), In: Patent Abstracts of Japan [CD-Rom].	1,9,19
A	FR 2 691 260 A1 (ABB CONTROL), 19 November 1993 (19.11.93), abstract; fig.1,2; claims 1-7.	1-22
A	EP 0 146 377 A1 (THE COMMONWEALTH OF AUSTRALIA), 26 June 1985 (26.06.85), abstract; fig.1,2; claim 1.	1-22

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
„A“ document defining the general state of the art which is not considered to be of particular relevance
„E“ earlier application or patent but published on or after the international filing date
„L“ document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
„O“ document referring to an oral disclosure, use, exhibition or other means
„P“ document published prior to the international filing date but later than the priority date claimed
„T“ later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
„X“ document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
„Y“ document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
„&“ document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 September 1999 (13.09.99)	16 September 1999 (16.09.99)

Name and mailing adress of the ISA/AT	Authorized officer
Austrian Patent Office Kohlmarkt 8-10; A-1014 Vienna Facsimile No. 1/53424/200	Berger Telephone No. 1/53424/453

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/KR 99/00304

Im Recherchenbericht angeführtes Patentdokument / Patent document cited in search report / Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung / Publication date / Date de publication	Mitglied(er) der Patentfamilie / Patent family member(s) / Membre(s) de la famille de brevets	Datum der Veröffentlichung / Publication date / Date de publication
JP A2 6337284	06-12-1994	keine - none - rien	
FR A1 2691260	19-11-1993	FR B1 2691260	01-07-1994
EP A1 146377	26-06-1985	AU A1 36822/84 AU B2 577339	20-06-1985 22-09-1988